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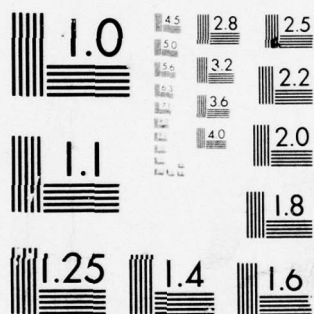
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⁹ TECHNICAL REPORT NO. 1

¹²

⁶ THE APPLICATION OF A DIPOLAR THEORY TO THE PIEZOELECTRICITY
IN VINYLIDENE FLUORIDE-CO-TETRAFLUOROETHYLENE POLYMERS.

by

¹⁰ Harry Stefanou

Prepared for publication

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The piezoelectric activity of eight vinylidene fluoride-co-tetrafluoroethylene polymers was studied to further our understanding of this phenomenon. Film compliance, density, degree of crystallinity, and piezoelectric activity were measured in this study. It is shown that the piezoelectric		

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→ d constant is calculable from a molecular dipole theory
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I. INTRODUCTION

The relatively high piezo- and pyroelectric activity of poly(vinylidene fluoride), PVDF, reported by Kawai^{1,2} has prompted a number of investigators to investigate the underlying causes. Several reviews on the piezoelectricity of polymers with emphasis on PVDF have been published.^{3,4} There is mounting evidence that the mechanism for the high activity in PVDF involves cooperative alignment of dipoles and/or charge trapping in the polymer film. Murayama,^{5,6,7} studying thermally stimulated depolarization currents, surface charges, and the dependence of the piezoelectric constants on morphological properties of poly(vinylidene fluoride), has concluded that trapped charges are responsible for the observed activity. Labes also favors trapped charges^{8,9} and has determined that the trapped charges originate from a Richardson-Schottky emission from the poling electrodes.¹⁰

The mechanism involving molecular dipolar contributions arises from the fact that of the three morphological forms,¹¹ designated α , β , and γ , that poly(vinylidene fluoride) can possess, the β phase (form I) has been shown to give the highest piezo- and pyroelectric activity. The β phase has orthorhombic $mm2$ symmetry with the CF_2 dipoles parallel to the crystallographic b axis.¹²⁻¹⁴ The symmetry and polar axis are necessary and sufficient to render form I poly(vinylidene fluoride) piezo- and pyroelectrically active.¹⁵ Several investigators have evidence that the polar axis of the crystals

can be coerced to lie parallel to an applied electric field.¹⁶⁻²¹ The parallel orientation of these dipoles leads to a residual polarization in the film²² that has been used to explain the piezo- and pyroelectricity through a variety of mechanisms.²²⁻²⁶

Poly(vinylidene fluoride) film as normally obtained from the melt is predominantly in the non-polar α form, and, despite the necessity for stretching the film in order to obtain the β phase, most of the major work, as outlined above, has used this homopolymer. However, it is known that as little as 7% by weight tetrafluoroethylene copolymerized with vinylidene fluoride will lead to a copolymer with crystals exclusively in the β form.²⁷ This obviates the necessity of stretching, although it is still desirable for enhanced activity, and removes the added parameter of having a polymer film with partial α phase content. Hence this copolymer system provides a good model for study. Several investigators have studied the piezo- and pyroelectric activity of the vinylidene fluoride-tetrafluoroethylene copolymer.^{6,28,29} Davis and Broadhurst³⁰ have used a dipole theory to calculate the polarization responsible for the piezoelectric d constant of the vinylidene fluoride-tetrafluoroethylene copolymer. In the present paper the vinylidene fluoride-tetrafluoroethylene copolymer system is discussed in detail. Six polymers of different composition synthesized in our laboratories and two copolymers, KYNAR 7200 and KYNAR 5200, made by a commercial Pennwalt process were used in this study. The piezoelectric activity is calculated from a molecular dipole theory and is shown to agree quite well with observed values.

II. EXPERIMENTAL PROCEDURES

A. Polymer Synthesis

The copolymers of vinylidene fluoride and tetrafluoroethylene were prepared by conventional latex polymerization procedures. The reaction was initiated at 84°C with the gradual addition of a sodium persulfate solution. The monomer mixture of proper proportions was fed to the reactor upon demand in order to maintain an isobaric condition at approximately 300 PSI. Upon completion of the reaction, the latex was coagulated with nitric acid. The coagulum was washed with distilled water in successive steps until the conductivity of the wash water was below 0.05 millimhos/cm. The washed powder was then dried and used to make compression molded films. Melt rheology of the samples proved that all the polymers were of high molecular weight.

B. Film Stretching

Compression molded films of the copolymers were uniaxially oriented by stretching to 400% strain. Although there was no necessity for converting α to β form as in the case of the vinylidene fluoride homopolymer, a uniform stretching operation was employed. All films were stretched at 100°C at an initial strain rate of 0.5 in./in.-min. Stretching began subsequent to a 10-minute preheat at 100°C and was followed by a 10-minute stress relaxation interval at the same temperature.

C. Poling

Poling of the copolymers was accomplished by applying Al foil electrodes to a 5 cm square of the uniaxially stretched films. This composite was then sandwiched between 2 brass electrodes. Voltage was applied incrementally until it was sufficient to create a 20×10^6 V/M field across the sample preheated to 90°C (see figure 1). The poling field was maintained for 90 minutes, the last 30 minutes being used to cool the sample with forced air. Subsequent to poling and prior to testing, the sample was placed between grounded electrodes and kept under approximately 40×10^3 Newtons of force for 12 hours. This latter procedure sufficed to remove most of the unstable polarizations on the film.

D. Testing of the Piezoelectric Activity

A Carver Press calibrated with a quartz pressure transducer was used to apply a compressional stress to the surface of the polymer film sandwiched between electrodes as described in the poling section (see figure 1). A Keithley electrometer was used to measure the charge output of the stressed films, and a piezoelectric stress coefficient was calculated.

III. EXPERIMENTAL RESULTS

In order to calculate the polarization due to dipole density from equation (1)³⁰

$$P = \left(\frac{\epsilon_\infty + 2}{2} \right) \frac{\mu}{V} \times \Psi_{xf} \quad (1)$$

the degree of crystallinity, x , and the average molar volume, \bar{V} , are needed. These can be calculated from the heat of fusion and density of the copolymer, respectively. In equation (1), μ is the dipole moment of vinylidene fluoride (2.1 D),³¹ x is the mole fraction of vinylidene fluoride in the copolymer, f is the fraction of head to tail polymerization (~ 0.9), and Ψ is the averaged dipole moment contributing to the polarization. Of course, the dipoles in the non-crystalline regions are thermally disoriented quite quickly after poling, because the glass transition of the copolymer is in the region of -30 to -40°C , and therefore make no contribution to the net polarization. Table 1 summarizes the heats of fusion measured in triplicate on a Perkin-Elmer Differential Scanning Calorimeter (Model 1B) coupled with an Infotronic's CRS-100 integrator. Also listed in the table are the degrees of crystallinity reported in mole per cent. The crystallinity is calculated from the ΔH_{fusion} and the ΔH_u of one mole of vinylidene fluoride crystals. For the ΔH_u , a value of 1425 cal/mole was used.^{32,33} The incorporation of tetrafluoroethylene units in the crystals is not expected to influence the calculation significantly because the ΔH_u is 1370³⁴ cal/mole. Also in Table 1 are the densities of the polymers measured by displacement in de-aerated water with a few per cent surfactant (ASTM D-792). These densities and the molecular weight of an average monomer unit were used to calculate the molar volume, \bar{V} (column 5 in Table 1).

A. Calculation of the d Constant

The method chosen to measure the d constants actually records

the charge (Q) accumulated on foil electrodes as a result of the applied stress. However, Q is given by equation (2):

$$Q = P \times A \quad (2)$$

in which P is the polarization per unit area, A. Differentiating equation (2) with respect to the vector component of stress results in the equation for the measured d constant.

$$\frac{\partial Q}{\partial \sigma_3} = A \frac{\partial P}{\partial \sigma_3} + P \frac{\partial A}{\partial \sigma_3} . \quad (3)$$

The subscript 3 denotes the direction perpendicular to the film plane and stretching direction. The convention for the designation of direction is diagrammed in Figure 2. The "1" direction is the direction of stretching and the "2" axis is in the plane of the film perpendicular to the "1" axis. Also the "internal microscopic coordinates" are shown. Here the "1" axis coincides with the draw direction and the "c" axis of oriented crystallites, and the "2" and "3" axes have the same directionality as the macroscopic axes, but represent the "a" and "b" axes of the crystallites (not necessarily respectively). However after the films are poled it is expected that the crystallographic b axis (dipole axis) will have a component parallel to the "3" direction. If we assume that the area of the Al electrodes is invariant, i.e., that $\partial A / \partial \sigma = 0$ then the measured piezoelectric constant, d_{33} , is given by

$$d_{33} = \frac{\partial Q/A}{\partial \sigma_3} = \frac{\partial P}{\partial \sigma_3} \quad (4)$$

The electrometer measures the value of Q , and we can calculate d_{33} from the imposed stress change.

B. Expression for $\partial P / \partial \sigma$

A calculation of $\partial P / \partial \sigma_3$ from basic principles would provide d_{33} values that could be compared to those experimentally obtained. A molecular dipole theory that was successfully applied to poly(vinyl chloride)³⁵ permits such a calculation to be made. Specifically, Broadhurst and Mopsik developed a theory for a glassy amorphous polymer the molecular dipoles of which were immobilized by cooling below the glass transition. When dipoles are immobilized while under the influence of an electric field, a permanent polarization results. An equation for this permanent polarization was derived using a cavity reaction field similar to that used by Onsager.³⁶ The pressure derivative of this equation agreed quite well with the hydrostatic d constant of poly(vinyl chloride), and the temperature derivative agreed with the pyroelectric constant. The reader is directed to reference 35 for greater details in the derivation.

In the present treatment the glassy polymer is replaced by semicrystalline vinylidene fluoride-co-tetrafluoroethylene polymer, and the pressure derivative that was used to calculate

the hydrostatic d constant is replaced by a derivative with respect to a specific component of the stress. The permanent polarization resides in the crystals of the polymer that exhibit a spontaneous polarization because of their dipole moment and orthorhombic symmetry. In all other respects the treatments are parallel. The equation for $\partial P / \partial \sigma$ which is taken from reference 35 is

$$\frac{\partial P}{\partial X} = -P \left\{ \frac{1}{V} \frac{\partial V}{\partial X} \left(1 + \frac{\epsilon_{\infty}^{-1}}{3} - (\epsilon_{\infty} + 2) \frac{D}{V^2} \right) + \frac{J_1(\phi_0)}{J_0(\phi_0)} \frac{\partial \phi_0}{\partial X} \right\} \quad (5)$$

in which P is the polarization, ϵ_{∞} is the high frequency limit of the dielectric constant, V is the volume, D is a constant used to correct the Clausius-Mossotti equation,³⁷ and $J_0(\phi_0)$ and $J_1(\phi_0)$ are Bessel functions of the first kind of zero order and first order, respectively, ϕ_0 is the librational amplitude of the oscillating dipoles, and X is a generalized stress variable (in our case σ_3).

Following the treatment by Mopsik and Broadhurst, we may regard as insignificant the terms involving D , and ϕ_0 is small because in an isothermal, variable stress experiment the Gruneisen constant used to approximate ϕ_0 will be small. Hence the simplified equation

$$\frac{\partial P}{\partial X} = -P \left\{ \frac{1}{V} \frac{\partial V}{\partial X} \left(1 - \frac{\epsilon_{\infty}^{-1}}{3} \right) \right\} \quad (6)$$

results. In contrast to the case in which a hydrostatic pressure

is applied to an isotropic polymer, the present system involves a specific component of the stress tensor applied to an anisotropic polymer film. The calculation of $\frac{1}{V} \frac{\partial V}{\partial X}$ although straightforward is worth outlining in detail.

C. The Calculation of $\frac{1}{V} \frac{\partial V}{\partial X}$

All the films in this study were uniaxially drawn and the resulting orthorhombic symmetry provides additional symmetry elements that reduce the number of independent terms in the compliance matrix to nine.³⁸ The matrix notation equation for the strain, ϵ_i , in terms of the stresses σ_i is:

$$\begin{bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \epsilon_4 \\ \epsilon_5 \\ \epsilon_6 \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} & S_{13} & 0 & 0 & 0 \\ S_{12} & S_{22} & S_{23} & 0 & 0 & 0 \\ S_{13} & S_{23} & S_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & S_{66} \end{bmatrix} \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} \quad (7)$$

in which the S_{ij} are the components of compliance.

The volume strain is given by

$$\frac{\Delta V}{V} = \epsilon_1 + \epsilon_2 + \epsilon_3 \quad (8)$$

in which from (7)

$$\begin{aligned}\epsilon_1 &= S_{11}\sigma_1 + S_{12}\sigma_2 + S_{13}\sigma_3 \\ \epsilon_2 &= S_{12}\sigma_1 + S_{22}\sigma_2 + S_{23}\sigma_3 \\ \epsilon_3 &= S_{13}\sigma_1 + S_{23}\sigma_2 + S_{33}\sigma_3.\end{aligned}$$

Because σ_1 and $\sigma_2 = 0$, equation (8) becomes

$$\frac{\Delta V}{V} = S_{13}\sigma_3 + S_{23}\sigma_3 + S_{33}\sigma_3. \quad (9)$$

Rearranging and introducing Poisson's Ratio $\nu_{ij} = -S_{ij}/S_{ii}$ gives

$$\frac{\Delta V}{V} = (1 - \nu_{13} - \nu_{23})\sigma_3 S_{33}. \quad (9A)$$

Using the values $\nu_{13} = 0.6$ and $\nu_{23} = 0.2$ as did Sussner for explaining anisotropic behavior in the vinylidene fluoride homopolymer³⁹ then yields

$$\frac{\Delta V}{V} = 0.2 S_{33}\sigma_3. \quad (9B)$$

To evaluate the volume strain, a value for S_{33} is needed. A value can be obtained by attributing the change in capacitance of a parallel plate capacitor to the change in thickness of the copolymer dielectric (3-direction) when the stress on the capacitor is normal to the electrodes (see figure 2). Again it must be assumed that $\partial A / \partial \sigma = 0$ and that the stress change does not cause a significant change in ϵ_∞ . The latter assumption can be tested by the expression^{35,37}

$$\frac{\partial \epsilon_{\infty}}{\partial \sigma} = - \frac{1}{V} \left[\frac{(\epsilon_{\infty} + 2)(\epsilon_{\infty} - 1)}{3} - \frac{D}{V^2} \frac{(\epsilon_{\infty} + 2)^2}{3} \right] \frac{\partial V}{\partial \sigma} \quad (10)$$

in which the term in D can be neglected. Using equation (9B) for $\frac{1}{V} \frac{\partial V}{\partial \sigma}$ and a value of $\epsilon_{\infty} = 3$ for the copolymers being considered results in equation (10A)

$$\frac{\partial \epsilon_{\infty}}{\partial \sigma} = \frac{10}{3} (0.2) (S_{33}) \quad (10A)$$

The compliance has an order of magnitude of $10^{-9} \text{ M}^2/\text{N}$ and $\Delta \sigma$ in these experiments was $2.79 \times 10^7 \text{ PA}$. Hence $\Delta \epsilon_{\infty} = 1.9 \times 10^{-2}$, which is indeed negligible. Thus the strain, ϵ_3 , accompanying the change of a stress, $\Delta \sigma_3$, is given by $\epsilon_3 = \frac{C_0}{C_f} - 1$ in which C_0 is the capacitance of the system containing the copolymer under test at the low stress level and C_f is the capacitance at the high level of stress. With these numbers the compliance $S_{33} = \Delta \epsilon_3 / \Delta \sigma_3$ is now calculable. Table 2 contains these values for each of the copolymers.

D. Calculation of the d Constant

Using equations 1, 4, 6 and 9B gives d_{33} as

$$d_{33} = - \frac{(\epsilon_{\infty} + 2)}{2} \frac{\mu}{V} \times \chi_f \Psi \left\{ 0.2 S_{33} \left(1 - \frac{\epsilon_{\infty} - 1}{3} \right) \right\} \quad (11)$$

Table 2 also contains the calculated value of d_{33} together with the values of the polarization calculated from equation (1).

It should be noted that Ψ was assigned a value of $1/3$ in keeping with the hypothesis that upon coercion from an applied field the dipoles are restricted to a 180° rotation in response to the torque.³⁰ Accompanying the calculated d_{33} are the observed values. The average difference of these values, $\bar{\Delta}$ is -1.01 and the standard deviation s is 2.5 . If the average difference represents a sample from an infinite population with mean $\mu = 0$, then the calculated d_{33} values are not different from those observed. The null hypothesis is that this latter statement is true. Using small sampling theory may disprove it if a Student's t value is calculated and shown to be larger than a critical value, t_c . The latter value is obtained from tables using the number of degrees of freedom and the desired level of significance.

$$t = \frac{\bar{\Delta} - \mu}{s/\sqrt{N}} = \frac{-1.01}{2.5/\sqrt{8}} = 1.16$$

Since $t_c = 1.90$ at the 0.05 level of significance, we cannot reject the hypothesis. Alternately, but not as rigorously, we may state that the calculated values for d are in agreement with the observed values.

IV. CONCLUSIONS

It has been shown that at the levels of piezoactivity observed in the vinylidene-co-tetrafluoroethylene polymers the piezoelectric d constants are a systematic function of the

compliance and degree of crystallinity of the polymers and that the total polarization and its stress dependence are adequately computed from the molecular dipoles using an Onsager cavity approach.

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TABLE 1

Measured Heats of Fusion and Densities. Calculated Degrees of Crystallinity and Molar Volume for Vinylidene Fluoride-co-tetrafluoroethylene Polymers.

<u>Mole % Vinylidene Fluoride</u>	<u>ΔH_{Fusion} (cal/gm)</u>	<u>Mole % Crystallinity</u>	<u>ρ (gm/cc)</u>	<u>\bar{V} (cc/mole)</u>
96	8.9 \pm .9	40	1.790 \pm .01	36.56
90	8.0 \pm .9	38	1.822 \pm .009	37.10
85	6.7 \pm 1.5	33	1.838 \pm .01	37.76
78	5.5 \pm .6	28	1.846 \pm .02	38.96
70	3.0 \pm .7	16	1.919 \pm .03	38.97
61	3.7 \pm .4	20	1.955 \pm .03	39.92
96 (KYNAR 5200)	8.6 \pm .3	39	1.809 \pm .03	36.17
78 (KYNAR 7200)	6.4 \pm .3	32	1.878 \pm .03	38.3

TABLE 2

Polarization, Compliance, Calculated and Observed Piezoelectric
d Constants for the Vinylidene Fluoride-co-tetrafluoroethylene Polymers

Mole % VF ₂	P (coul/m ²)	S ₃₃ (m ² /N)	-d ₃₃ (pC/N, from Eq. 11)	-d ₃₃ (pC/N, observed)
96	2.22 x 10 ⁻²	4.7 x 10 ⁻⁹	7.0	8.5
90	1.95 x 10 ⁻²	6.15 x 10 ⁻⁹	8.0	5.8
85	1.57 x 10 ⁻²	4.05 x 10 ⁻⁹	4.2	8.3
78	1.18 x 10 ⁻²	8.6 x 10 ⁻⁹	6.8	6.2
70	6.06 x 10 ⁻³	6.05 x 10 ⁻⁹	2.5	2.3
61	6.45 x 10 ⁻³	7.4 x 10 ⁻⁹	3.2	2.1
96	2.18 x 10 ⁻²	6.6 x 10 ⁻⁹	9.6	11.6
78	1.38 x 10 ⁻²	4.8 x 10 ⁻⁹	4.4	9.0

FIGURE CAPTIONS

Figure 1: Sample-electrode configuration showing Al and brass electrodes sandwiching the polymer sample.

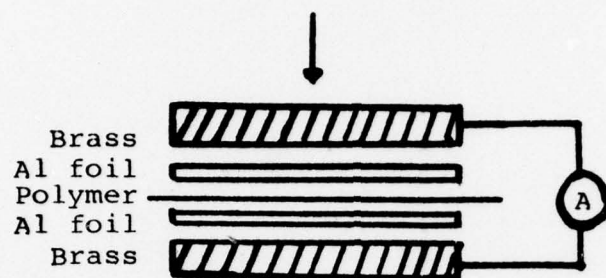
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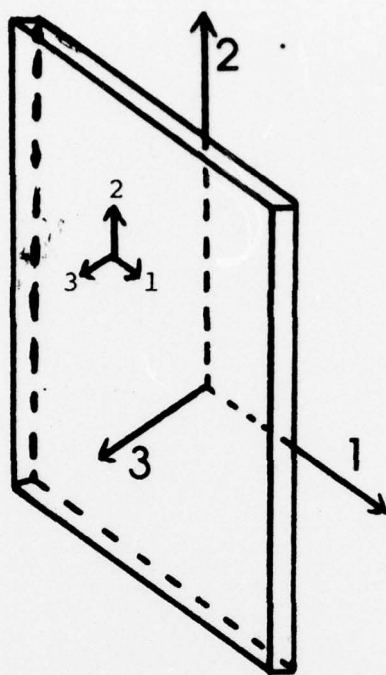
a voltage supply, the configuration is for
poling.

an electrometer and $\Delta\sigma_3 \neq 0$, the configuration
is for a d_{33} test.

an ECD capacitance meter and $\Delta\sigma_3 \neq 0$, the con-
figuration measures the capacitance as
a function of stress.

Figure 2: The macroscopic and microscopic coordinates used
to designate directionality in the uniaxially
oriented copolymer films.





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